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DIRECT OBSERVATION OF STRESS-INDUCED SHIFTS IN CONTACT POTENTIALS*

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The effect of stress on contact potential has been measured semiquantitatively in Al, Cu, Au, steel, and brass using a high-sensitivity version of the Kelvin method. The observed shifts are in all samples positive (i.e., the electric field outside the sample is more positive when pressure is applied) and the magnitude is a few microvolts per kg/cm² applied stress. Both sign and magnitude agree with the theories of Dessler, Michel, Rorschach, and Trammell, and of Herring, provided one assumes that gravitationally produced stress is equivalent to hydraulically produced stress.

Considerable interest has developed in the last few years in the existence of electric fields associated with metals in a gravitational field. Most of this interest stems from the magnificent series of experiments performed by Fairbank and Witteborn designed to investigate the gravitational force acting upon electrons and, eventually, upon positrons.¹ The most striking result of these experiments is the observation that free electrons located inside a conductive tube appear not to feel gravity.

This result has led to a number of theoretical papers. Schiff and Barnhill² showed how the gravitational potential acting upon the mobile electrons in the surrounding metals produces a downward shift in the electron distribution precisely large enough to yield a downward electric field which produces an upward force on electrons just sufficient to cancel the gravitational force. In this model conventional positrons will be accelerated downward with a force of $2g$. Later Dessler *et al.*³ showed that if one takes into account gravitational compression of the lattice as well as of the electron gas, the predicted potential is of opposite sign (i.e., positive potential at the bottom of the column) and a factor of roughly 10^4 larger. The precise magnitude involves the relative compressibilities of the lattice and of the electron gas. Herring⁴ has reached a similar conclusion based upon investigation of stress-induced shifts in work function. Particular models have been investigated by Peshkin⁵ and by Barnhill.⁶

Experiments of Witteborn and Pallesen⁷ in apparent disagreement with the theory of Dessler *et al.* have been criticized by Tannhauser⁸ and by Michel.⁹ Evidence supporting Dessler *et al.* and

Herring was found by Beams,¹⁰ who substituted a centrifugal potential for the gravitational potential and was able to observe an effect of the predicted magnitude and sign. In this experiment the potential at the outer rim of a centrifuge was compared with that at the center.

The theories of the gravitationally induced emf in metals all appear to assume local thermodynamic equilibrium within the metal. If this is the case, then the potential outside of a particular element of metallic surface depends only upon local conditions in the metal. In this case the origin of local stress in the metal is not in itself important. No difference would be expected upon substituting an externally applied compression for the gravitationally produced stress.

The present experiment accepts this viewpoint and utilizes a hydraulic press to supply compressions equivalent to hundreds of meters of material in a gravitational field. The parameter I have chosen to measure is the pressure-induced shift in contact potential. The main complication in relating an externally measured contact potential to interior properties of the metal arises in the complexity of the surface layers, with their equivalent dipole sheets.^{3,4,11} The strength of the method is that a noncontacting measurement of the electric field outside of a metal surface would appear to sense a property very similar to that which influences the electrons in the Witteborn-Fairbank experiment.

Noncontacting measurements of the small shifts expected are feasible using the Kelvin technique for measuring contact potentials.^{11,12} The apparatus is shown in Fig. 1.¹³ A brass reference electrode is vibrated at a distance of about a millimeter from the sample face, thereby producing

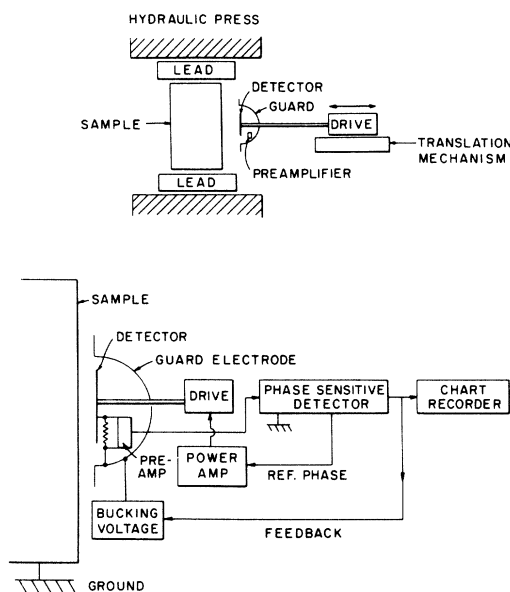


FIG. 1. The ac Kelvin method. The sample and guard are vibrated at about 150 Hz. The guard electrode is held at the same potential as the detector. The field-effect transistor first stage of amplification is mounted inside the guard to minimize capacity and the effects of triboelectricity. Sensitivity exceeds 100 μ V shift in contact potential and is limited entirely by changes in the properties of the surfaces under study.

a time-dependent change in capacitance. Charge entering or leaving the plate is converted in a resistor to an alternating voltage, which is amplified and phase-sensitively detected. A six-decade precision adjustable voltage source (General Resistance Co. Dial-A-Volt) can be adjusted so as to cancel the electric field in the gap due to the contact potential. To verify that the electric field is indeed zero, the entire transducer can be translated so as to change the gap spacing. In practice the output of the phase-sensitive detector is usually connected in series with the Dial-A-Volt, producing a closed-loop self-balancing system.

The samples used in most of the measurements were machined $2 \times 3 \times 2\frac{1}{2}$ -in.³ blocks of metal. These were sandwiched between lead sheets in an effort to equalize the applied stress, and placed in a hydraulic press. In other experiments strips of width $1\frac{1}{2}$ in. and thickness typically 0.010 in. were stressed in a tensile machine. No significant difference between the results of the two techniques was found. The stresses applied to the samples were limited to a few percent of the elastic yield limit. The experiments to date are intended to yield qualitative answers, and therefore

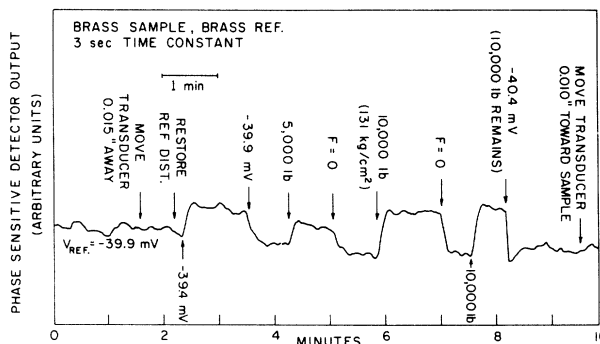


FIG. 2. Effect of stress on contact potential of brass. The output of a phase-sensitive detector is shown as the system is perturbed in various ways. The contact potential is neutralized with -39.9 mV. The balance is verified by moving the transducer. The calibration is determined by shifting the bucking voltage by 500μ V. The deflection due to 5000- and 10 000-lb force (65.6 and 131 kg/cm^2 pressure, respectively) is determined. Finally, the deflection due to 10 000 lb is balanced with -40.4 mV, and the existence of zero electric field verified by translating the detector.

no attempt was made to treat specially the sample surfaces beyond washing them with alcohol.

Measurements have so far been made on samples of Al, Cu, brass, Au, and steel. A portion of a chart recorder trace for the brass sample is shown in Fig. 2. The steps correspond to the application and removal of stresses of 65.5 and of 131 kg/cm^2 (total forces of 5000 and 10 000 lb, respectively) and to changes in the bucking voltage source of 500μ V and of 1 mV. The bucking supply voltage of -39.4 mV represents the contact-potential difference between the brass sample and the brass reference electrode. Note that the reference electrode must be made more negative to restore balance following application of stress, thus showing the shift to be positive. (The feedback loop is open in this run.)

The experimental results are summarized in Table I. The representative contact-potential differences shown are relative to the brass reference electrode and are variable depending on the condition of the surfaces.¹⁴ The third column of the table converts the observed shifts into a form suitable for comparison with the theories. In calculating these entries the applied stress is assumed to arise not from the hydraulic press but rather from a column of the material under investigation sufficiently high to yield the applied stress. The measurements are expressed as the number of microvolts shift in contact potential per meter of material. The resulting numbers

Table I. Shifts in contact potential observed under pressure. The first column presents typical values of voltage required to produce zero field between the brass reference electrode and the sample. The second column gives observed ranges of (positive) shifts in contact potential per unit stress, and the last column gives the predicted shift which would be produced by a column of material 1 m high. The measurements typically show variability from run to run of about a factor of 3, which arises from variability of the surface condition of the samples.

	Typical observed contact potential relative to brass (mV)	Shift in contact potential ($\mu\text{V cm}^2/\text{kg}$)	Equivalent gravitationally induced shift (see text) ($\mu\text{V}/\text{m}$)
Al	+628	1.4-5.7	0.38-1.5
Cu	-295	3-7.2	2.6-6.2
Brass	-39	4.6-7.4	4-6.4
Steel	-202	9.6-10	7.6
Au	-390	1.4-3.7	2.7-7.2

lie for all samples in the approximate range of 1-10 $\mu\text{V}/\text{m}$.

The theoretical predictions including compression of the lattice may be concisely (although approximately) expressed in terms of a parameter γ defined essentially as the ratio of the compressibility of the electron gas to that of the lattice³:

$$E = \frac{Mg\gamma}{e} \left(1 - \frac{m}{M\gamma}\right),$$

where M is the ionic mass and m is the electronic mass. For metals, γ is approximately unity; so the predicted field is (neglecting the influence of the surface dipole layers) of order microvolts/meter. The theory of Herring⁴ yields essentially the same result. Taking into account the substantial uncertainties in the theories (and particularly the difficult problem of the effect of stress upon the surface dipole layer) the agreement must be considered excellent.

Although Beams¹⁰ quotes no experimental numbers, he does assert agreement with the theory of Dessler *et al.* There thus appears to be agreement between his measurements and these. Both types of measurements were made with sample stresses orders of magnitude in excess of those applicable to the Witteborn and Fairbanks experiments. If any nonlinear effects are in operation, there would be no reason to expect the results to be in any manner comparable.

In view of the apparent discrepancy of about four orders of magnitude as well as the sign between the experiments of Witteborn and Fairbanks and those reported here, speculations directed toward the resolution of the dilemma seem in order. I would like to propose one such mechanism here. It is based on the observation that while the contact potential outside a sample varies with compression of the lattice as well as of

the electrons, the electronic work function is related to the chemical potential and varies within a system of connected metals only through the change $\Delta = mgh$ in gravitational potential of the electrons.⁴

This suggests that it is possible to shield the stress-induced contact potential by placing over the sample surface an unstressed surface layer in electrical contact with the sample. Since the chemical potential of the unstressed surface layer is independent of stress applied to the bulk sample, the contact potential immediately outside such an unstressed surface layer would be that of the surface layer material plus the term mgh . Such an unstressed surface might be prepared by attaching to the sample surface small conducting particles sufficiently far apart that no stress could be transmitted from particle to particle and yet close enough that the contact potential outside the surface would be controlled by the particles. Preliminary measurements utilizing Al small particles deposited on Au substrates do indeed show results substantially smaller than those of Table I.

Although the required neutralization of the lattice effects is formidable—exceeding 10^4 —it is possible that the specially prepared amorphous copper surface used by Witteborn and Fairbank may satisfy the requirements. In any event, the concept of an unstressed conductive surface layer acting as a shield offers a consistent mechanism for reconciling the variety of experimental observations.

A most helpful conversation with C. Herring is acknowledged. The efforts of V. Radeka and R. Chase were essential to the development of the instrumentation. The small particles of Al and Au were prepared by J. Crow. The success of the experiment owes much to R. Johnson and

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DETECTION OF FOREIGN ATOM SITES BY THEIR X-RAY FLUORESCENCE SCATTERING*

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The position of a solute atom in a lattice can be detected by the nature of its x-ray fluorescence excitation during a diffraction process.

The determination of the interstitial or substitutional nature of impurity atoms in crystalline solids has been given impetus recently because of particle channeling experiments. We wish to report here a rather direct method of determining the lattice position of a foreign atom by observing the fluorescence emitted by the atom during a diffraction process. Although the method, as illustrated by the present experiment, is limited to particular combinations of solute atoms and host lattices, in principle it can have much wider application.

When an incident beam is Bragg reflected by a reasonably perfect crystal, a standing-wave pattern is set up in the crystal which causes a change in the field intensity at a lattice site with respect to the average field of the incident plane wave when no diffraction takes place. This effect, which is explained by a two-beam dynamical theory, is responsible for the anomalous transmission or Borrmann effect in x-ray transmission. In this transmission case, a nodal plane of the electric field forms at the atom sites and the cross section for photoelectric loss (which is the primary absorption process) is reduced drastically. In the reflection case, as the incident angle increases from values smaller than the Bragg angle, there is a reduction of intensity at the atom sites resulting in a node of in-

tensity when the region of total reflection is reached. On the high-angle side of this region, there is an antinode of the field intensity at the atom site which gradually reduces to the incident-beam plane-wave values at large angles of incidence.

The nodal plane is precisely that which would be formed by the superposition of two plane waves in space such that wavelength (λ) and angle between their propagation directions (2θ) are related by Bragg's law, $\lambda = 2d_{hkl}\sin\theta$, and the spacing of the planes d_{hkl} is just the spacing of the nodal planes.

At certain interstitial sites for particular reflections the node-antinode situation will be reversed with respect to a lattice site. Hence, by observing the fluorescence of characteristic radiation from the solute atom as a function of Bragg angle, the location of the solute can be determined.

To demonstrate these ideas experimentally we used a highly perfect silicon single crystal heavily doped with arsenic.¹ The resistivity was 0.002 Ω cm and corresponded to an arsenic concentration of about 5×10^{19} cm⁻³. The experimental arrangement shown in Fig. 1 was similar to a previous experiment² used to detect the fluorescence from the host lattice and thus demonstrate the presence of the nodal and antinodal